AFC Fuels Development Update: 2003 Semi-Annual Meeting

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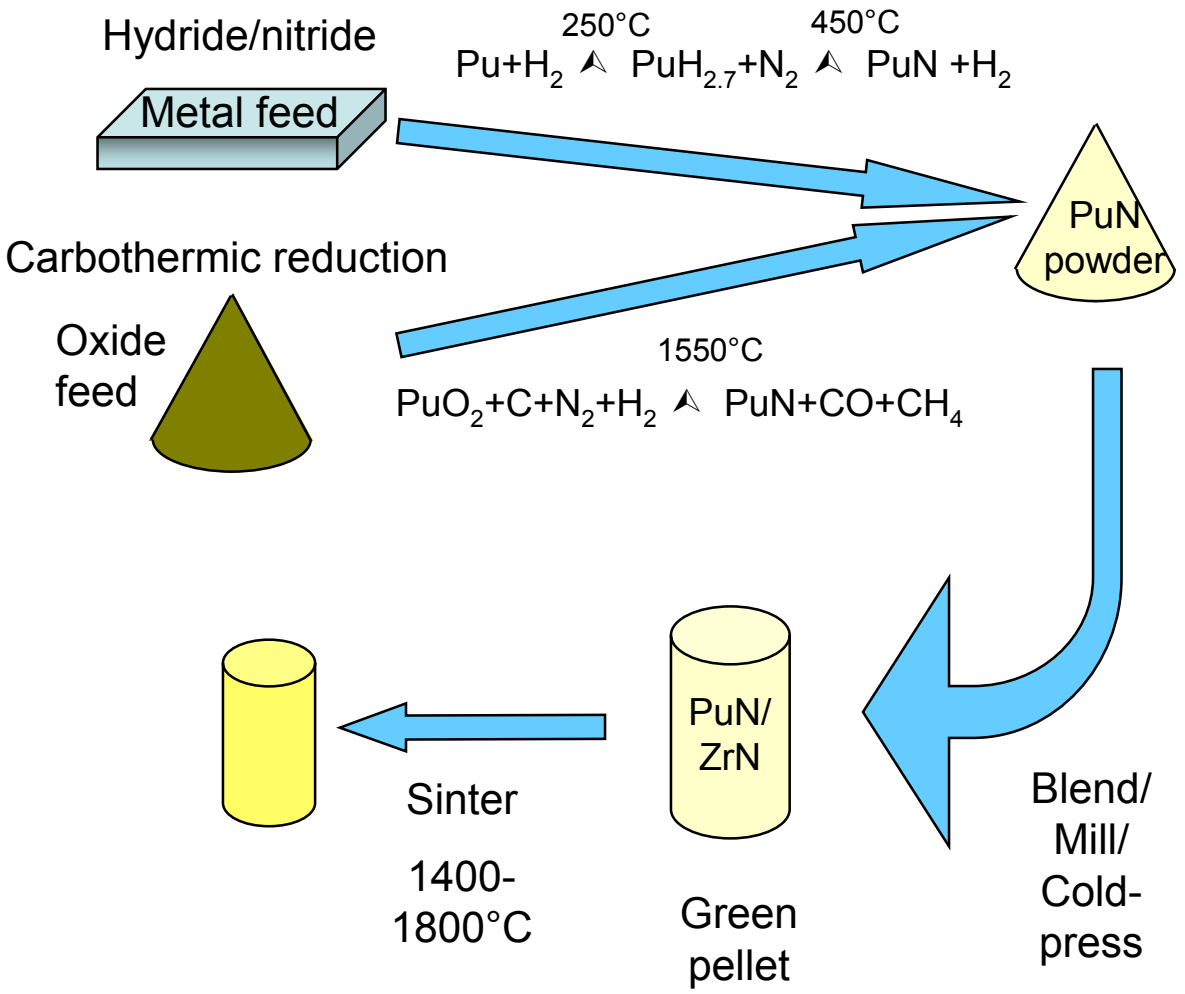
C-AAC: Debbie Dale, Randy Drake, and Dave Gallimore
MST-8: Ken McClellan, Kurt Sickafus, G. Egeland, J. Valdez, Marius Stan, Petrica Cristea, Anders M.N. Niklasson, Srinivasan, G. Srivilliputhur, and Michael I. Baskes
Arizona State U.: Pedro Peralta
Imperial College: Robin W. Grimes and Kurt J. W. Atkinson

Nitride pellet synthesis



PuN, AmN and NpN Synthesis

Synthesized by carbothermic reduction:

$$(Pu, Am\ or\ Np)O_2 + (2+x)C + \tfrac{1}{2}N_2 + 2xH_2 \rightarrow$$
$$(Pu, Am\ or\ Np)N + 2CO + xCH_4$$

	Pu	Am	Np
Reaction T (°C)	1550	1400	1550
Times reacted	1	3	1
Predicted weight loss (%)	17.95	17.95	17.95
Measured weight loss (%)	17.60	17.76	20.50

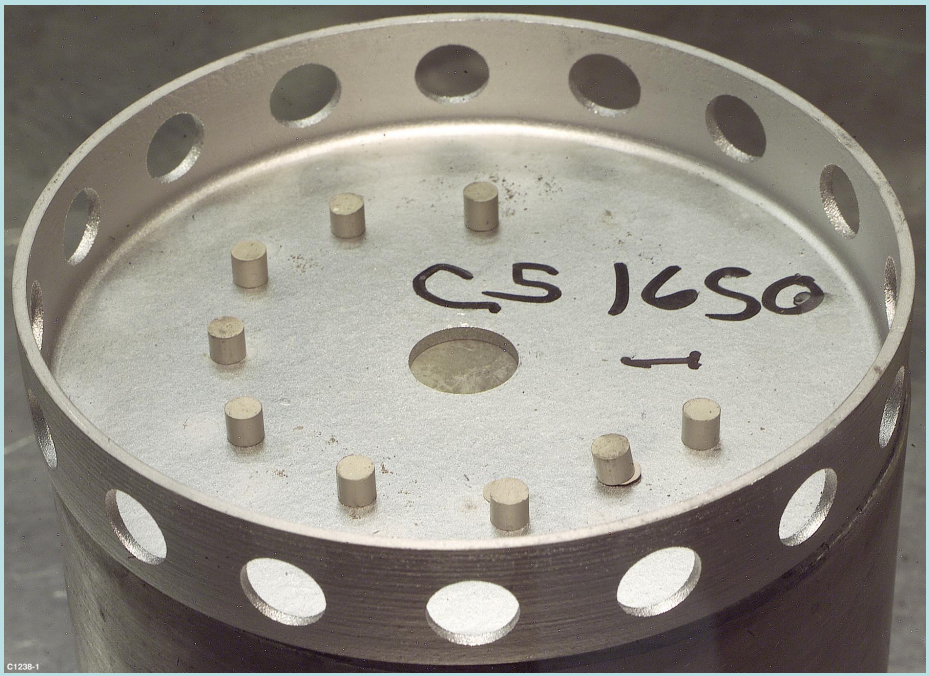
Nitrides for ATR Insertion

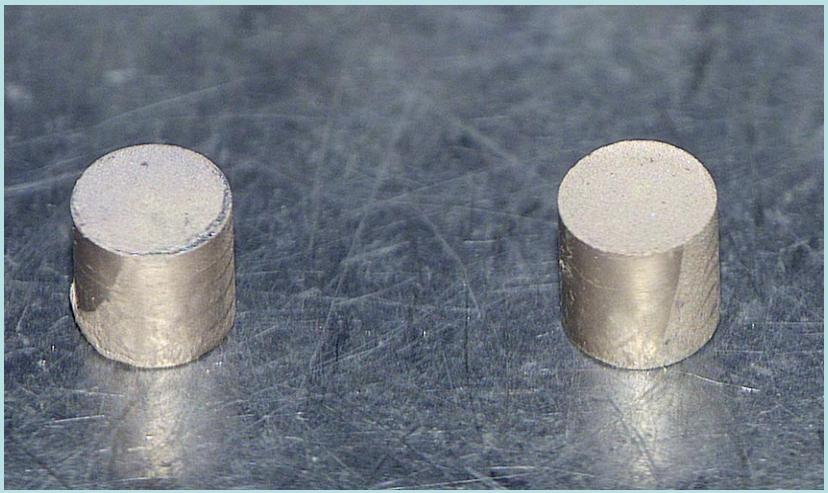
Comp	Target Composition	Sintering Conditions	Pellets fabricated	Density achieved
1	$(Pu_{0.2},Am_{0.8})N$-36ZrN	1550°C/ 10 hr./Ar	100%	65-75%
2	$(Pu_{0.8},Am_{0.2})N$-36ZrN	1650°C/ 10 hr./Ar	100%	80-85%
3	$(Pu_{0.5},Np_{0.5})N$-36ZrN	1700°C/ 10 hr./Ar	100%	80-90%
4	PuN-36ZrN	1700°C/ 10 hr./Ar	100%	80-90%
5	$(Pu_{0.5},Am_{0.25},Np_{0.25})N$-36ZrN	1650°C/ 10 hr./Ar	100%	80-85%
6	$(Pu_{0.5},Am_{0.5})N$-36ZrN	1600°C/ 10 hr./Ar	~50%	65-75%

Sintering conditions chosen to optimize Am retention (the higher the Am content, the lower the sintering T)

Nitride pellet fabrication

Production of Comp 5 ($Pu_{0.5}$, $Am_{0.25}$, $Np_{0.25}$)N-36ZrN pellets sintered at 1650°C

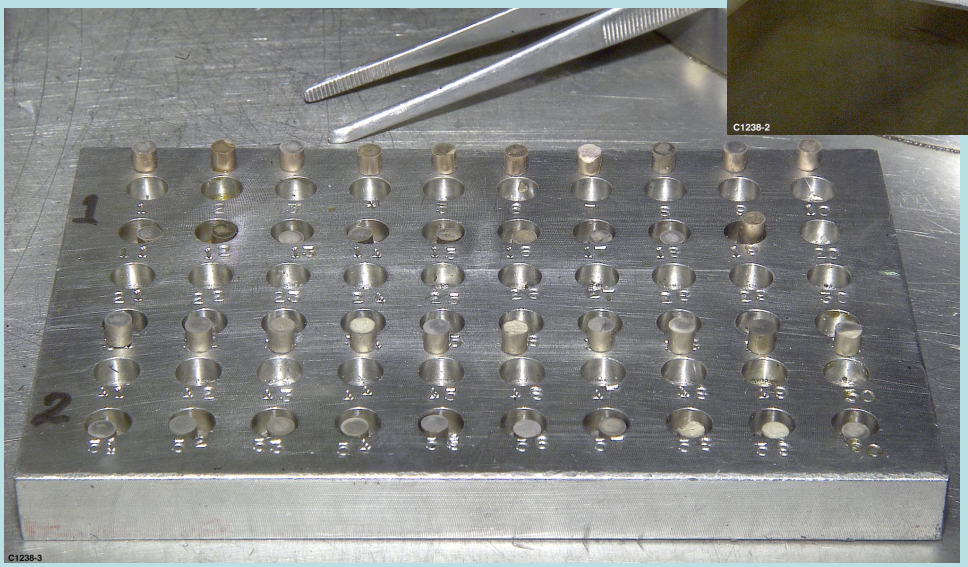




Production of Comp 4 PuN-36ZrN pellets sintered at 1700°C

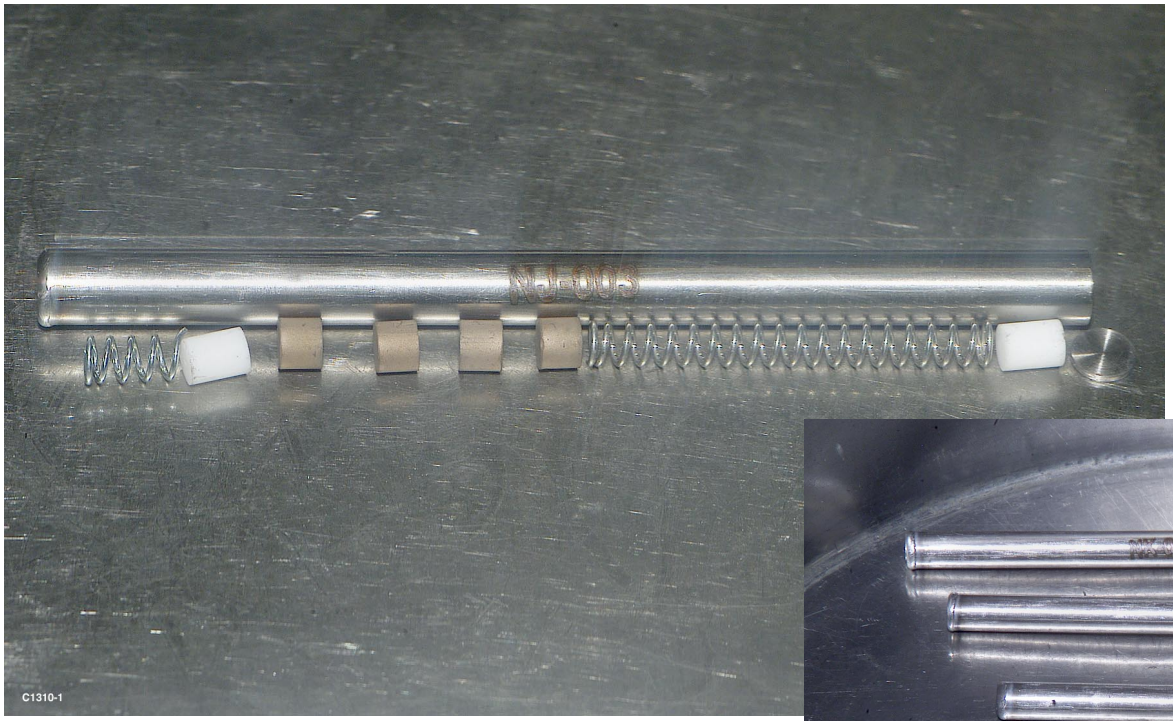
ATR nitride pellet production

Compositions
3 and 4

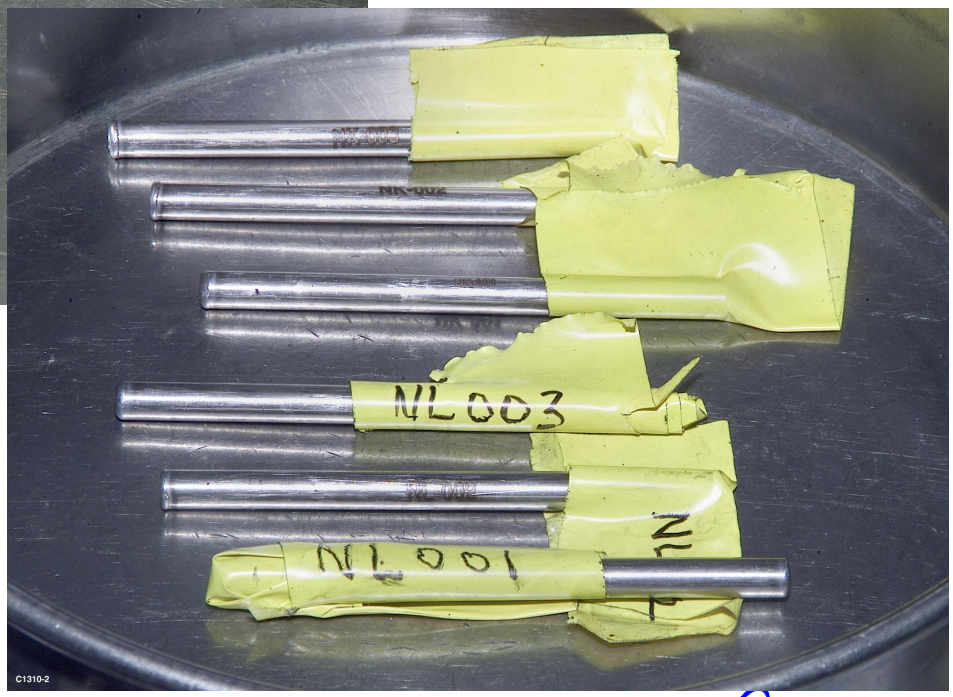


Compositions
1, 2, 5 and 6

Pellets loaded into shipping containers



Assembly of nitride pellets into shipping vessel



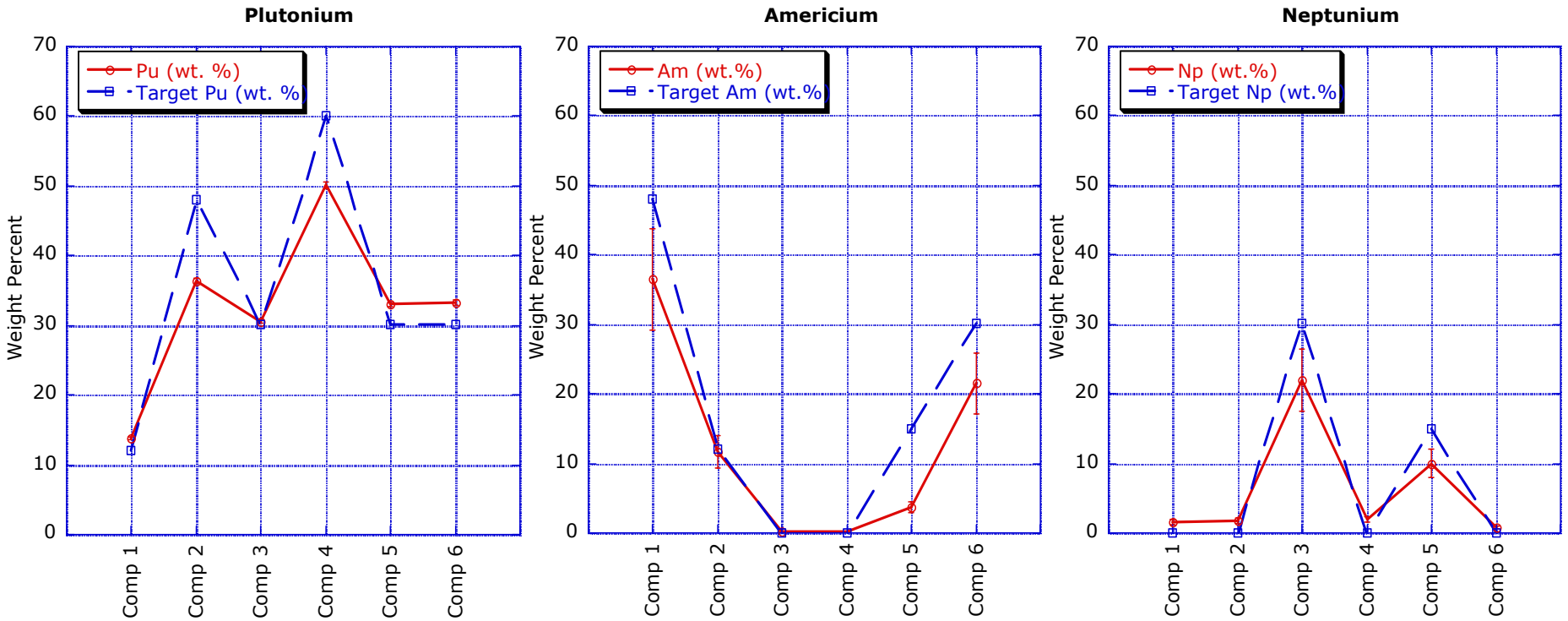
Six shipping vessels with two compositions awaiting welding

Pu Isotopics for ATR Nitrides

Isotope	Comp1	Comp2	Comp3	Comp4	Comp5	Comp6	Average	Feedstock value
Pu 238 (wt.%)	0.0101	0.0095	0.0118	0.0099	0.0107	0.0100	0.010	0.009
Pu 239 (wt.%)	93.7975	93.8662	93.8843	93.8729	93.8717	93.8746	93.861	93.902
Pu 240 (wt.%)	6.0569	5.9905	5.9725	5.9845	5.9833	5.9820	5.995	5.969
Pu 241 (wt.%)	0.1057	0.1051	0.1035	0.1048	0.1057	0.1050	0.105	0.096
Pu 242 (wt.%)	0.03	0.0286	0.0278	0.0278	0.0286	0.0284	0.029	0.024
Pu 242 (wt.%)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

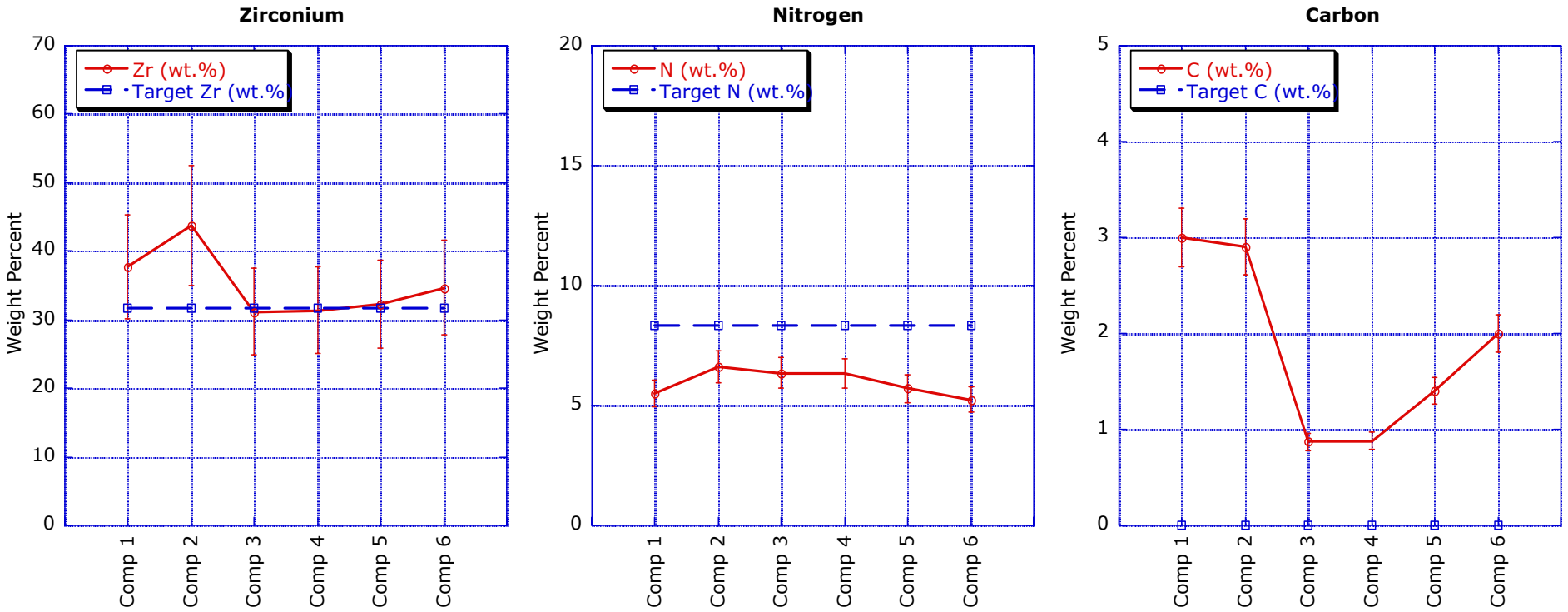
- *One Pu oxide feedstock used for all PuN synthesis*
- *Very little variation in isotopics from Comp to Comp*
- *Rich in Pu-239*

Actinide Contents for ATR Nitrides



- *All actinides boiled off to some extent*
- *Am loss similar to Pu loss*
- *Complicated vaporization behavior*

Chemistry of other constituents for ATR Nitrides



- *Zr loss was minimal*
- *N loss indicates possibly N-deficient nitride, still rocksalt nitride*
- *High C contents because of excess C added (C-to-oxide molar ratio of 3.1-to-1.0)*

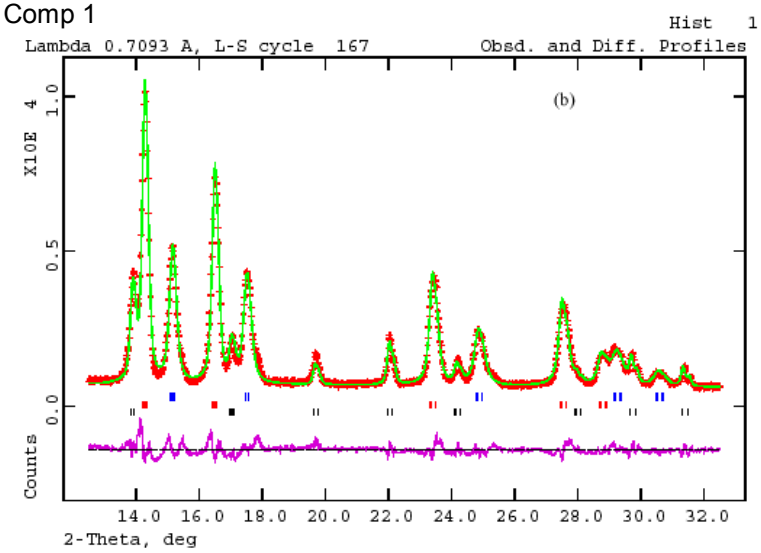
Composition change due to actinide vaporization

	Target Composition	Sintering Conditions	Pellet Weight loss (%)	Resulting Composition
1	$(Pu_{0.2},Am_{0.8})N$-36ZrN	1550°C/ 10 hr./Ar	8.7	$(Pu_{0.27}Am_{0.70}Np_{0.03})$-43ZrN
2	$(Pu_{0.8},Am_{0.2})N$-36ZrN	1650°C/ 10 hr./Ar	2.0	$(Pu_{0.73}Am_{0.24}Np_{0.04})$-50ZrN
3	$(Pu_{0.5},Np_{0.5})N$-36ZrN	1700°C/ 10 hr./Ar	0.8	$(Pu_{0.58}Np_{0.42})$-36ZrN
4	PuN-36ZrN	1700°C/ 10 hr./Ar	2.0	$(Pu_{0.96}Np_{0.04})$-36ZrN
5	$(Pu_{0.5},Am_{0.25},Np_{0.25})N$-36ZrN	1650°C/ 10 hr./Ar	6.0	$(Pu_{0.71}Am_{0.08}Np_{0.21})$-37ZrN
6	$(Pu_{0.5},Am_{0.5})N$-36ZrN	1600°C/ 10 hr./Ar	9.7	$(Pu_{0.60}Am_{0.39}Np_{0.01})$-39ZrN

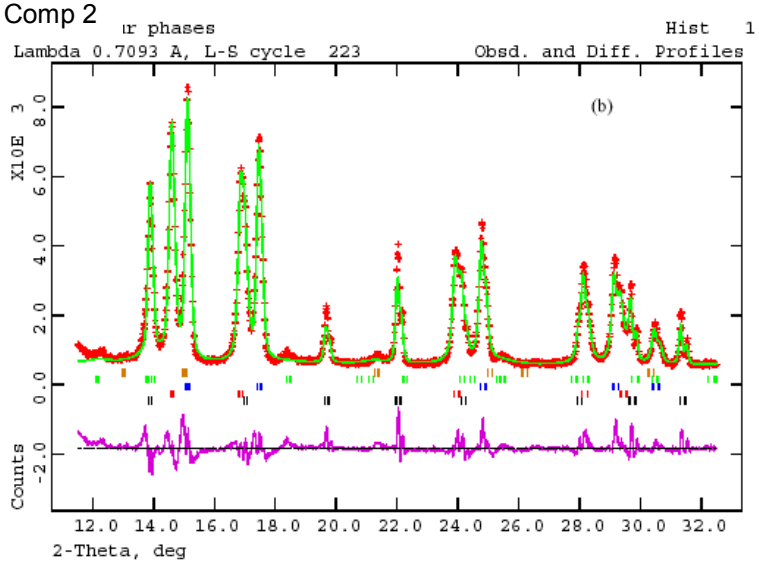
- *Sintering temperature chosen based on Am content*
- *Actinide content remained at 64 wt.% or decreased*

X-ray diffraction for ATR nitirdes

Comp 1



Comp 2



- *Only one crystal structure, rocksalt, was identified*
- *No free metal and little oxide observed*
- *Usually two rocksalt structures with differing lattice parameters was observed*
- *Suggests the incomplete interdiffusion of actinide nitride with zirconium nitride*

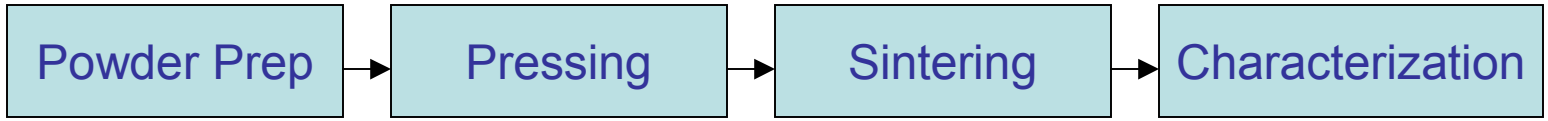
Before Sintering

ZrN 4.61 A	PuN 4.91 A

After Sintering

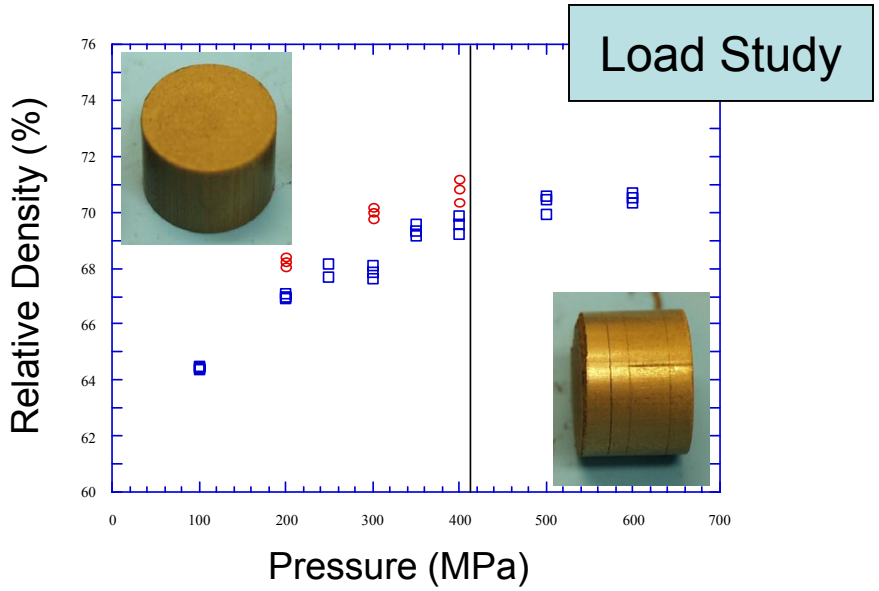
ZrN 4.61 A	(Pu-Zr)N 4.76 A	PuN 4.91 A

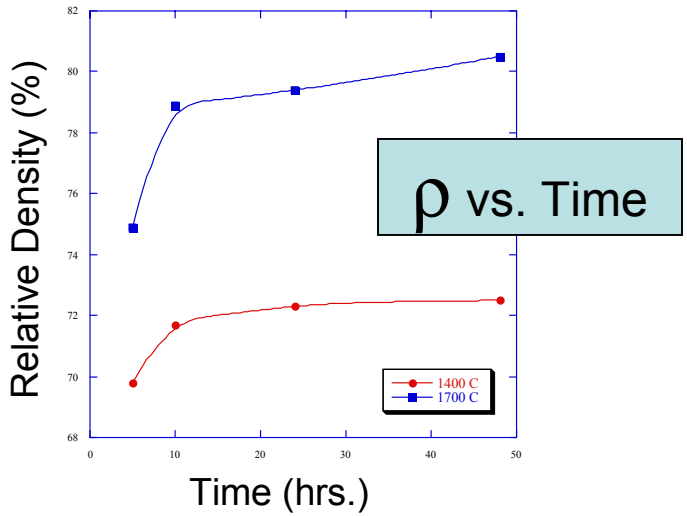
Cold ZrN Processing

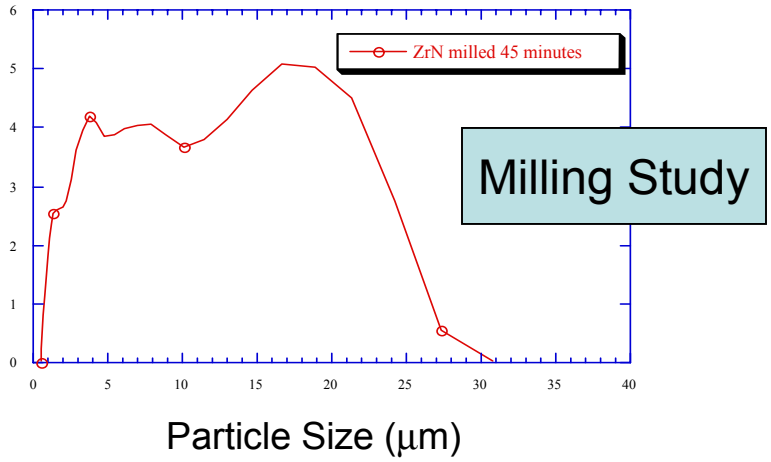


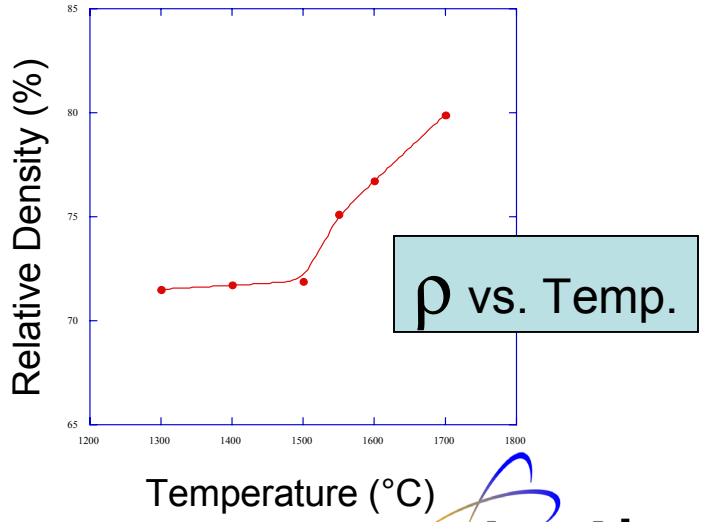
	Powder Prep	Pressing	Sintering	Characterization
Recent Studies	•Milling Study •Die Lubricant	•Press Load Study	•Sintering Aid * •Density vs. Time •Density vs. Temperature	•Particle Size
Defined Parameters	•Density change optimized at 45 min. mill time •Synthetic lube	•Best combination of green density and pellet quality at 400 MPa	•Densification of ZrN activates above 1550°C and >10 hrs.	•Mill study established preferred particle size of <10 μm.

ZrN Processing Results









Fuel Processing Goals (ZrN and UN)

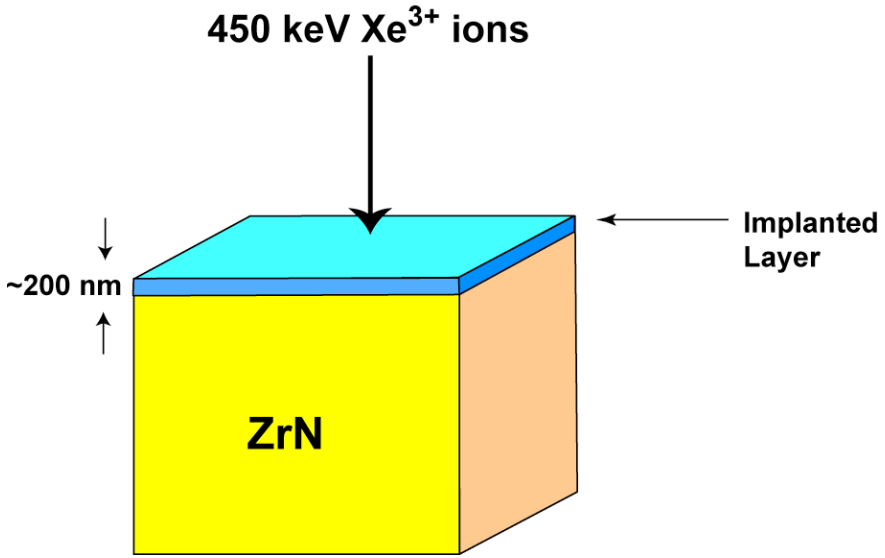
Recent Additions

- New double workstation glovebox
- Authorization to process depleted uranium

Near Term Goals

- Sintering aid study
- Lattice parameter study (DU as surrogate)
- Phase II low fertile fuel development

Radiation Damage Experiments on Polycrystalline ZrN

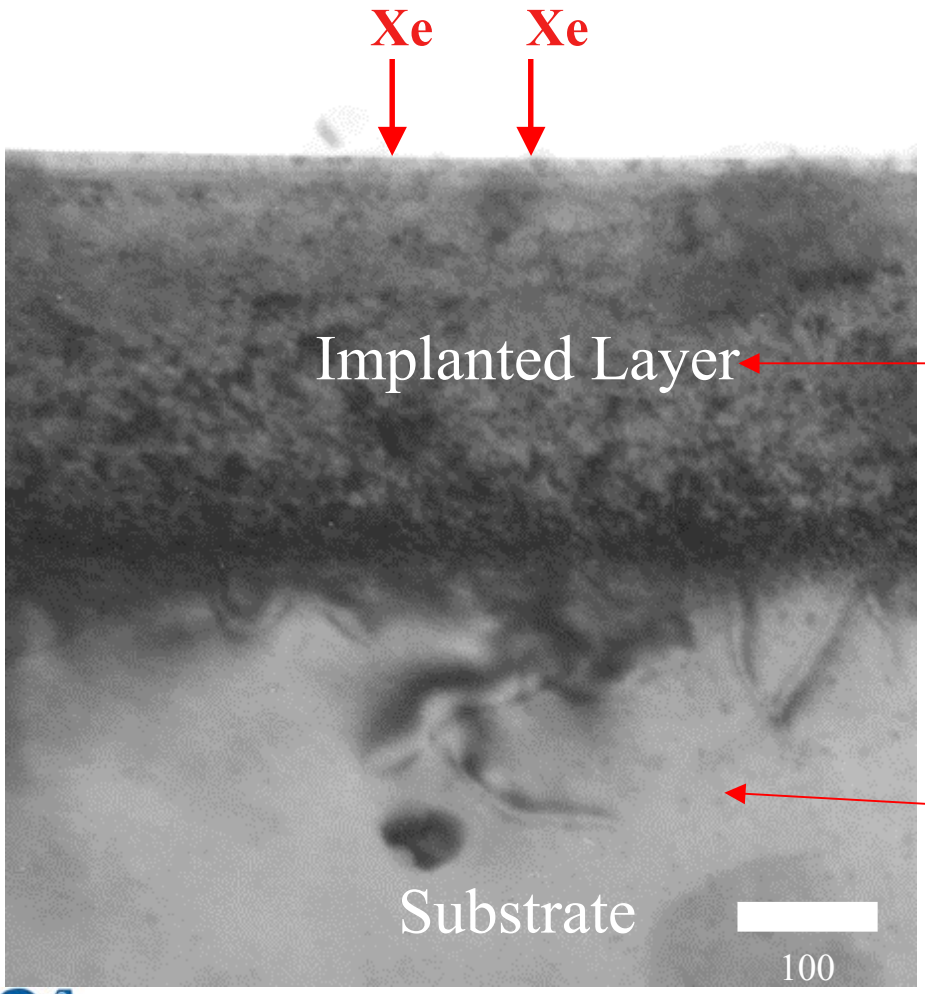


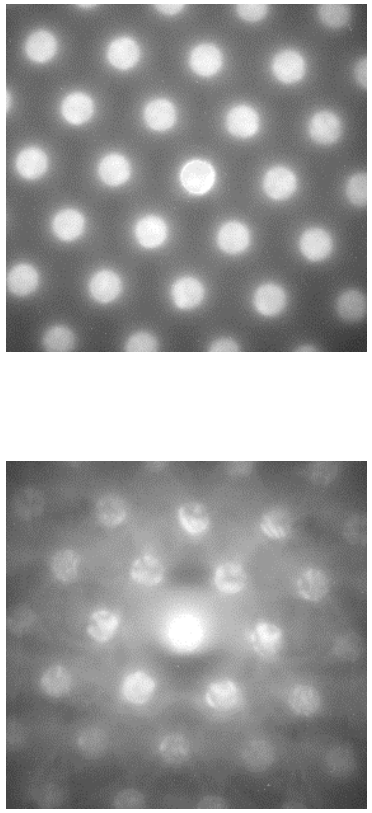
ZrN samples were irradiated at ~100K with Xe ions to evaluate radiation damage evolution following irradiation with heavy ions.

450 keV Xe^{3+} ions were used for the Xe ion irradiations.

Cross-sectional Transmission Electron Microscopy and Micro-Diffraction from Xe Ion-Irradiated ZrN

450 keV Xe^{++} ions, fluence = $2 \cdot 10^{16}$ Xe/cm^2, peak dose ~ 80 displacements per atom (dpa)

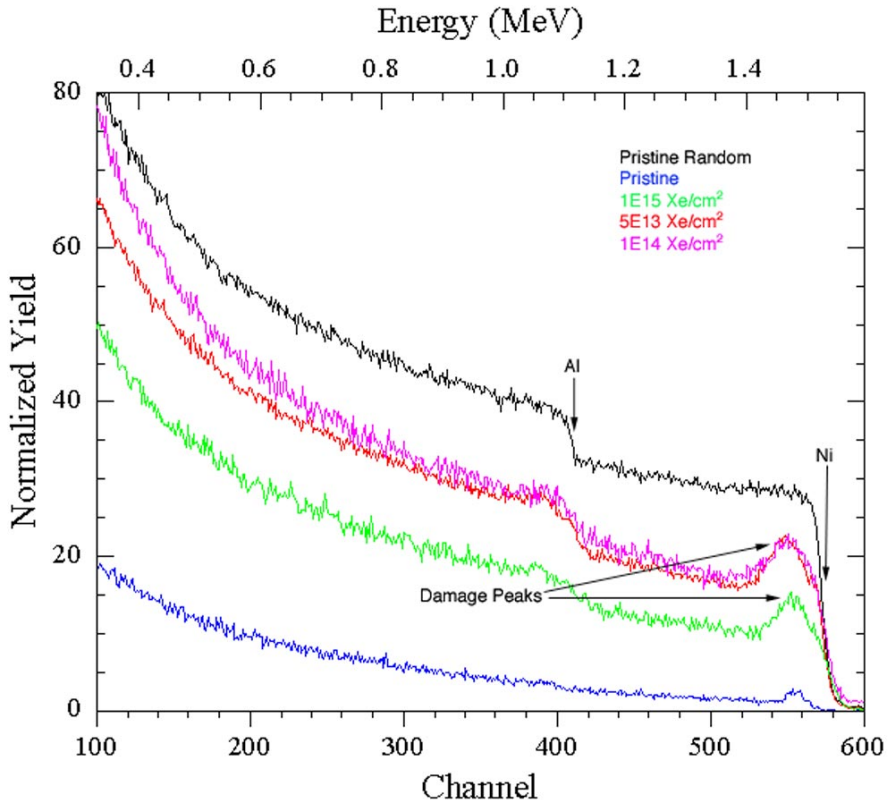




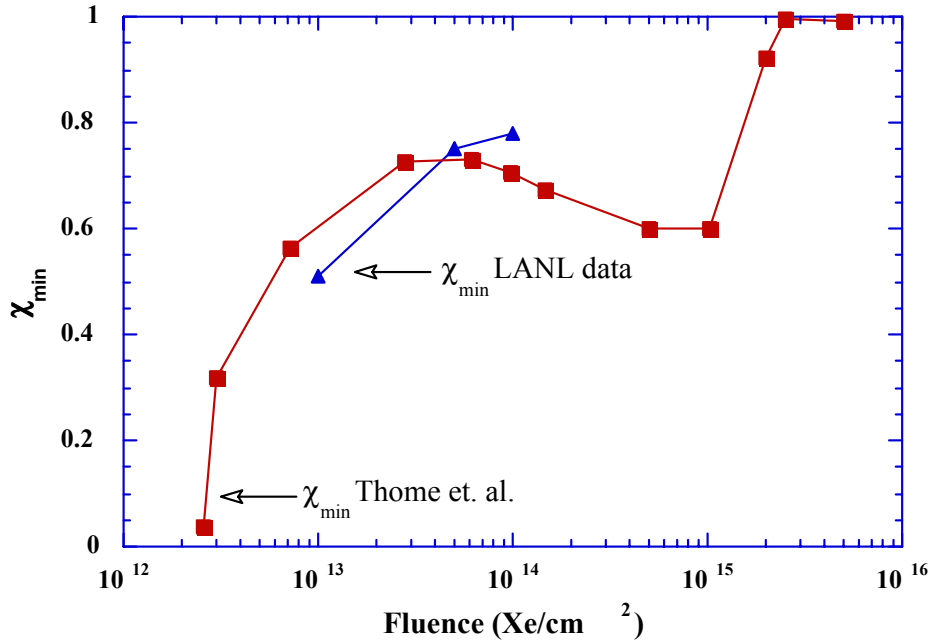
No change in crystal structure to 80 dpa

Radiation Damage Evolution in Single Crystal NiAl

A single crystal NiAl sample was irradiated under cryogenic conditions (~100K) with 450 keV Xe^{++} ions to fluences of $1•0^{13}$, $5•10^{13}$, and $1•0^{14}$ Xe/cm^2. Samples were examined using Rutherford backscattering / ion channeling (RBS/C) following Xe ion irradiation.



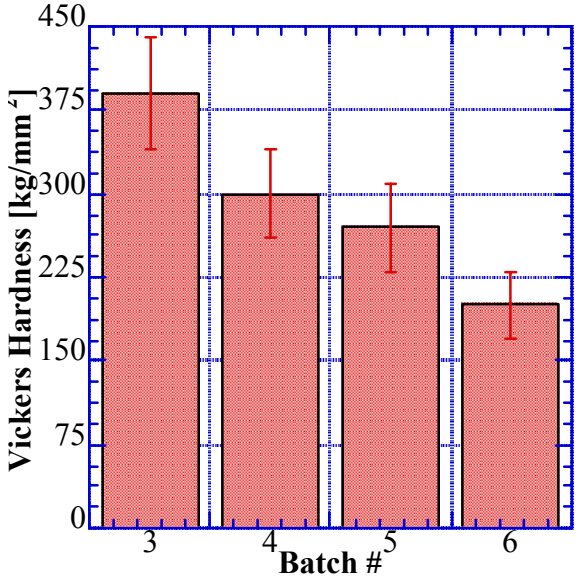
Radiation Damage Evolution in Single Crystal NiAl



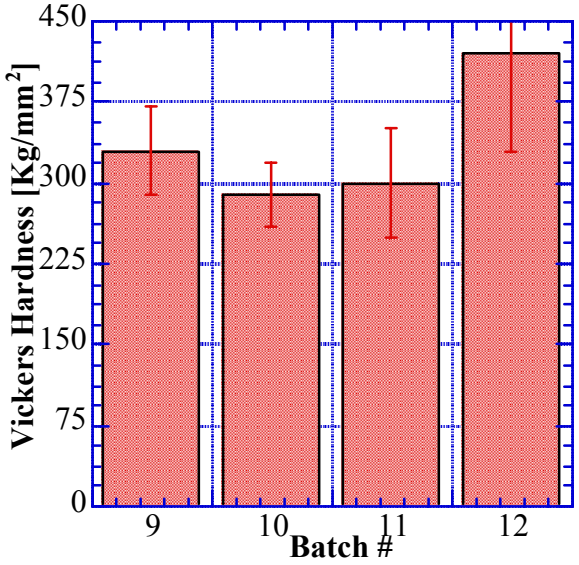
Comparison between the damage accumulation factor, χ_{min}, for RBS/C data obtained by Thomé et al. on 360 keV Xe^{++} ion irradiated NiAl at 90 K versus LANL obtained following irradiation with 450 keV Xe^{++} at 100K. The agreement between the measurements is excellent.

The rate of damage accumulation was observed to decrease dramatically with increasing fluence. The damage remained almost unchanged between fluences $5 \cdot 10^{13}$ and $1 \cdot 0^{14}$ Xe/cm^2; i.e., retained damage remained constant even though the displacement dose was doubled.

Microhardness of ZrN



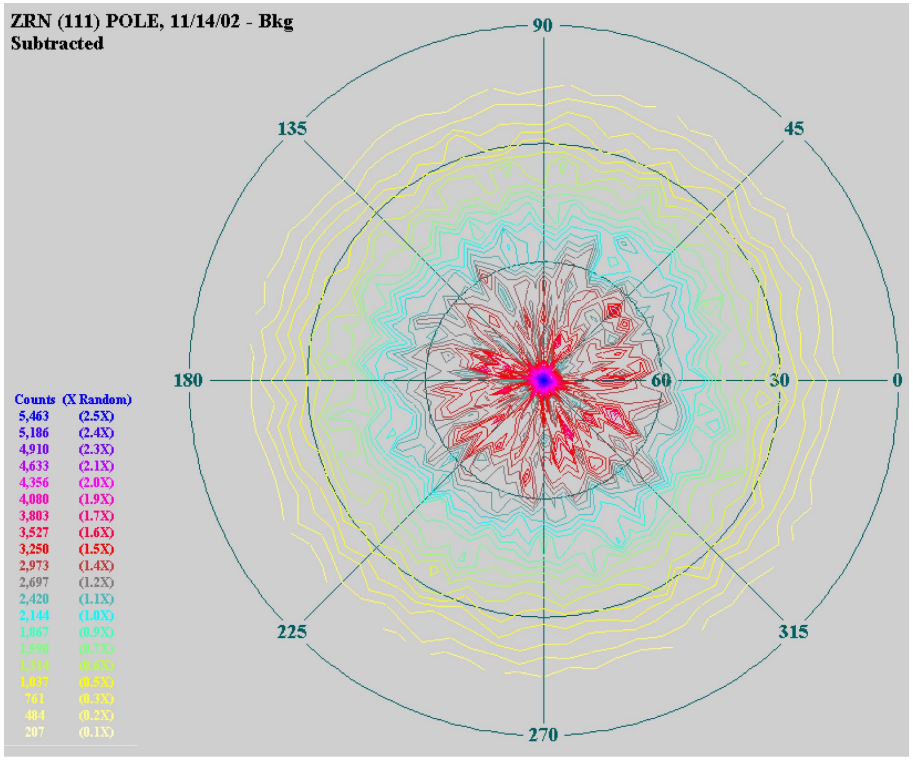
Old Sintering Process



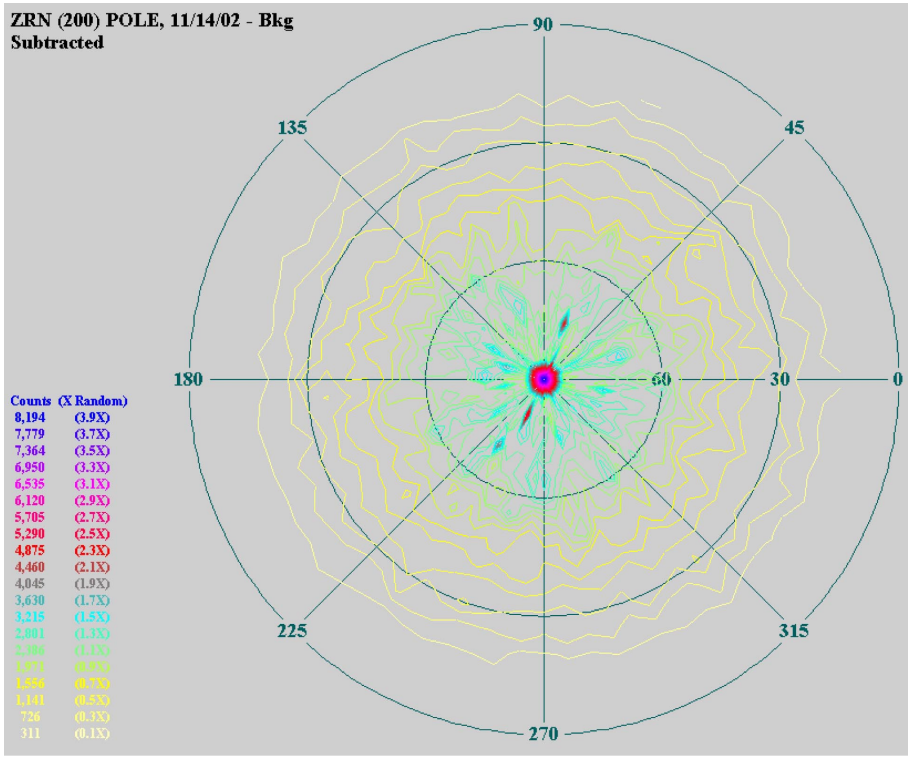
New Sintering Process

- *The average hardness of the material is 20% higher for the new sintering process*
- *The hardness values are much more uniform across different batches for the new process*
- *The new process leads to higher strength and reliability*

Crystallographic Texture of ZrN



Weak, non-uniform (111) fiber texture



Strong, uniform (200) fiber texture

- *Texture leads to anisotropic behavior, which can be beneficial.*
- *However, the mechanisms of texture formation need to be studied before it can be used.*

Mechanical Behavior Anisotropy

- Hardness on radial and longitudinal planes is about the same: it is controlled by porosity
- Fracture toughness presented different values on radial and longitudinal planes, with $K_{Icradial} > K_{Iclong}$

The sample width is ≈ 1 mm

Crack path on the radial plane.

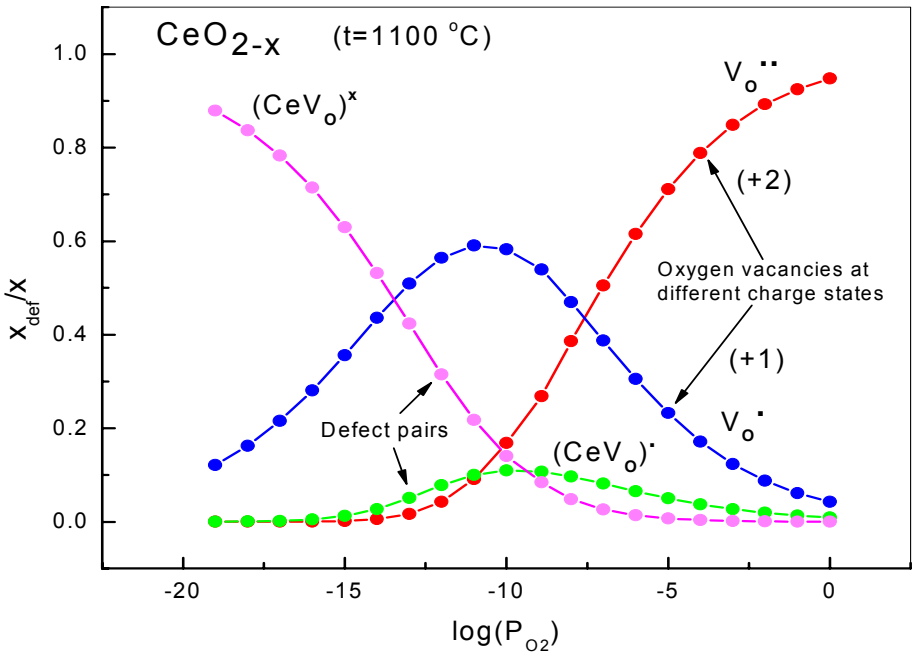
Crack path on the longitudinal plane.

Rougher crack path on the longitudinal plane resulted in lower K_{Ic}. More information on monolithic ZrN is needed to understand this behavior

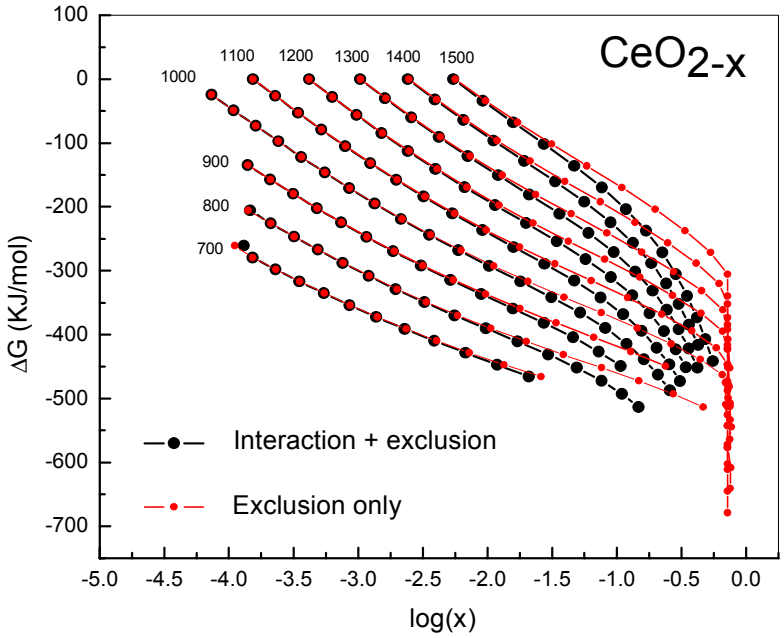
Modeling of Defect Chemistry in CeO_{2-x}

- The concentration of defect species in CeO_{2-x} was calculated for various temperatures and oxygen pressures.
- The calculated partial free energy of formation (per mol of O_2) of CeO_{2-x} will be used for phase equilibrium calculations and simulation of oxygen diffusion.

After validation, the model and simulations will be further extended to PuO_{2-x} and UO_{2-x}.

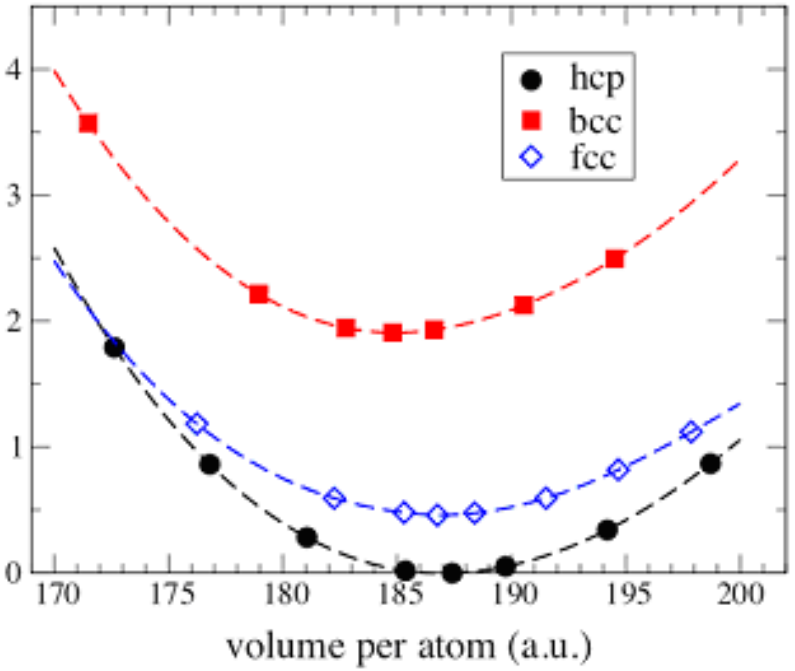


Normalized defect concentration in CeO_{2-x} at 1100 ºC.



Excess Gibbs free energy of CeO_{2-x}.

Atomistic Modeling of Americium



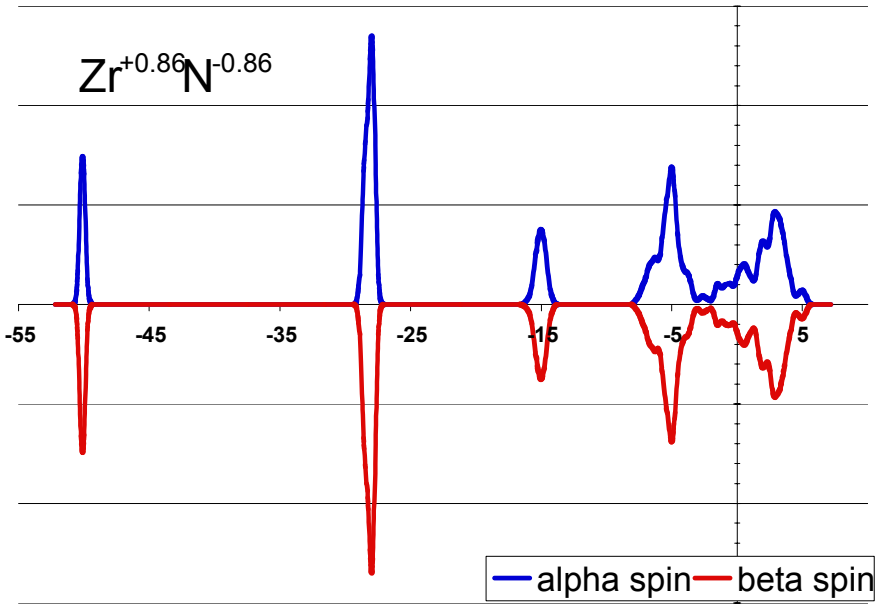
Energy versus volume for BCC, FCC, and HCP phases of Am.

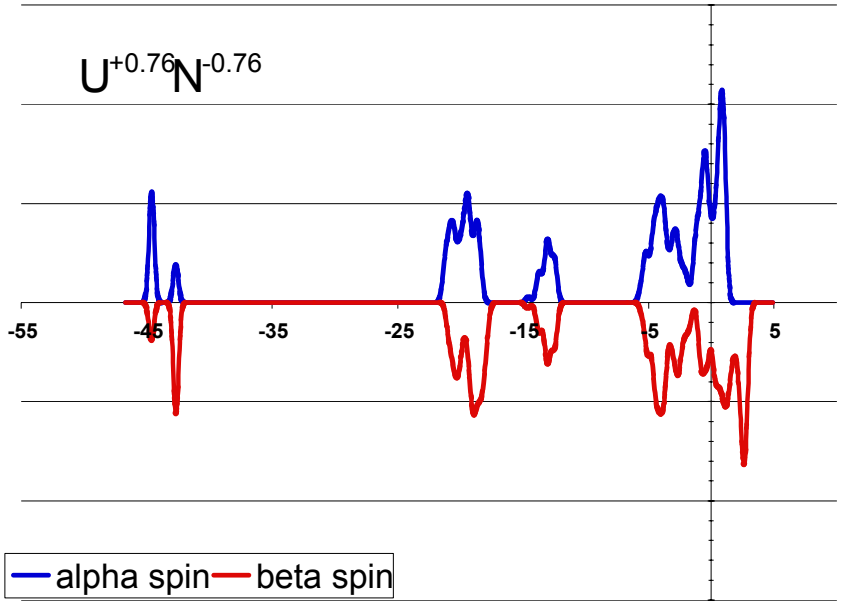
- First Principles calculations resulted in values of lattice constants, bulk modulus, cohesive energy, and vacancy energy.
- A Modified Embedded Atom (MEAM) potential for Am was optimised.
- Similar results for AmN are in progress.

The goal is to model the properties of AmN, with impact on thermo-mechanical calculations in the Pu-Am-N system.

Atomic Scale Simulation of Nitride Fuel

- The observed structures and predicted ionic character of ZrN and UN are very similar.
- The calculated densities of states show distinct differences.
- As a consequence there will be differences between:
  - their bond energies
  - the associated physical/electronic properties.





These calculations are presently being extended for the solid solutions and the results feed directly into the thermodynamic calculations.

Summary

- Nitrides for ATR fabricated and shipped
  - Chemistry completed (except oxygen)
  - Compositions/densities fairly close to desired values
  - Pu Isotopics: ~94% Pu-239, ~6% Pu-240
- Cold fuel development effort
  - Extensive development on fabrication parameters for ZrN
  - Authorization for work on depleted uranium
  - Mechanical properties of ZrN improved when sintered with N
  - ZrN remains crystalline and rocksalt at 80 dpa
  - Modeling efforts show progress toward development of integrated fuel behavior models